PATENT SPECIFICATION (11) 1395958

(21) Application No. 38515/72 (22) Filed 17 Aug. 1972
(31) Convention Application No. 63928/71 (32) Filed 21 Aug. 1971 in
(33) Japan (JA)
(44) Complete Specification published 29 May 1975
(51) INT CL² G03C 5/30
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(19)

(54) PROCESS AND COMPOSITION FOR DEVELOPING SILVER HALIDE PHOTOLITHOGRAPHIC MATERIAL

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for producing a photolithographic plate used for the graphic arts and, in particular, to a litho-developer composition for producing a photolithographic plate.

To produce a photolithographic plate used for the graphic arts, a litho-type photosensitive material for producing half-tone dots or line drawings or high-contrast photosensitive material by which images having very high contrast and excellent sharpness are formed have generally been used.

A half-tone printing plate can be produced by exposing a lithotype photosensitive material to an image of an original through a contact or cross-hatched screen and developing the material with a litho-developer composition to obtain high-contrast development, the stability of the developer composition is very inferior to that of the common monochromatic developer composition. Attempts have been made to improve the stability by adding an antioxidant other than sulphite, but it has not been possible to obtain a developer composition having as good stability as in an ordinary monochromatic developer composition.

The litho-type photosensitive material has previously been developed by plate development but since this is complicated, treatment using an automatic developing apparatus has been carried out recently. When using an automatic developing apparatus, the treating ability of the developer is kept uniform by adding a supplemental amount of the developer composition for every treatment of the photosensitive materials. However, it is necessary to adjust the quantity added of the supplemental developer composition according to the size of the photosensitive material to be treated and the blackened area thereof. When the developer composition is left overnight in the tank of the automatic de-

ERRATA

SPECIFICATION No. 1,395,958

Page 1, line 17, *after* or *insert* a
Page 2, line 57, *for* on *read* of
Page 3, line 41, *for* hydrophilic *read* hydrophobic
Page 3, line 75, *after* as *insert* saponin so as
Page 5, line 8, *after* mixture *insert* of viscosity about 3500 cPs
Page 5, line 46, *for* 200,00 *read* 200,000
Page 5, line 97, *after* 12 *delete* or

THE PATENT OFFICE
18th August, 1975

SEE ERRATA SLIP ATTACHED

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To produce a photolithographic plate used for the graphic arts, a litho-type photosensitive material for producing half-tone dots or line drawings or high-contrast photosensitive material by which images having very high contrast and excellent sharpness are formed have generally been used.

A half-tone printing plate can be produced by exposing a lithotype photosensitive material to an image of an original through a contact or cross-hatched screen and developing the material with a litho-developer composition.

It is preferable that the half-tone printing plate consists of dots having a maximum density and a background having a minimum density. However, areas having an intermediate density, the so-called fringe, are produced around the dots, because even the high-contrast photosensitive material has an intermediate density; this fringe is undesirable for the graphic arts, because it causes a considerable deterioration of the quality of the printing images. The quality of the half-tone dots is an important characteristic of a photolithographic plate used for the graphic arts.

The term "litho-developer composition" means an alkaline treating solution containing a known dihydroxybenzene-developing agent and, e.g., an aldehyde-alkali hydrogen sulphite addition salt as a preservative (so-called infectious developer). Since a litho-developer composition of this kind includes a small amount of free sulphite ions so as to obtain high-contrast development, the stability of the developer composition is very inferior to that of the common monochromatic developer composition. Attempts have been made to improve the stability by adding an antioxidant other than sulphite, but it has not been possible to obtain a developer composition having as good stability as in an ordinary monochromatic developer composition.

The litho-type photosensitive material has previously been developed by plate development but since this is complicated, treatment using an automatic developing apparatus has been carried out recently. When using an automatic developing apparatus, the treating ability of the developer is kept uniform by adding a supplemental amount of the developer composition for every treatment of the photosensitive materials. However, it is necessary to adjust the quantity added of the supplemental developer composition according to the size of the photosensitive material to be treated and the blackened area thereof. When the developer composition is left overnight in the tank of the automatic developing apparatus, it is necessary to add a large amount of the supplemental developer composition to bring the sensitivity thereof back to its initial level, because the stability of the developer composition is very inferior and the sensitivity deteriorates greatly; accordingly, the replenishment requires a long period of time, because the developer composition should be examined by using a previously exposed control strip before fresh developer is added.

Although the sensitivity recovers due to the addition of the supplemental developer composition, the quality of the dots and the half-tone gradation related to the tone reproduction of the original do not return completely to the level obtained using the fresh developer composition. It is therefore impossible to retain a uniform treating ability. This tendency increases as the period of use increases. Further, if the litho-developer com-

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position is left as it is for more than two days, the sensitivity and quality of the half-tone dots do not recover at all even if a large amount of the supplemental developer composition is added, and, consequently, black spots appear. The above described situation is well known in the industry. Treatment of these photosensitive materials can be carried out only by a person who has acquired a large amount of experience over a long period of time, and now much attention and time are required for controlling such a development.

Further, during use of such a developer which is continually replenished, materials dissolved from the photosensitive material and the oxidation products of the developer accumulate in the solution to cause the formation of scum and a deterioration of the treating ability.

Formation of half-tone dots by the litho-developer depends to a large extent upon the degree of agitation of the developer composition; in general, dots of better quality can be obtained when the agitation is carried out gently. Accordingly, the quality of the dots obtained using an automatic developing apparatus is very different from that obtained using another automatic apparatus in which the character of the agitation is different. It is rarely the case that the intended quality of the developed photosensitive material is obtained, because the litho-developer composition is very sensitive to the pH and the developer composition has a different property each time it is prepared by the user. In practice, even if a photo-sensitive material having the same quality is used, variation results, depending on the conditions and the method of treatment employed by the user.

It is therefore an object of the present invention to provide a treating process by which the defects accompanying the treatment of litho-type photosensitive material by known litho-developers are alleviated and more uniform properties are obtainable.

We have found that the above described problems can be substantially overcome by developing an exposed litho-type photosensitive material using a viscous litho-developer composition which contains an agent which increases the viscosity of the developer composition (hereinafter for brevity designated a "viscosity-increasing agent"). to at least 1000 centipoises measured at 25°C.

The viscous litho-developer composition of the invention can be applied to the surface on an exposed photosensitive material at a specific thickness; the application can be made from a hopper or tube of the composition through a narrow slit or nozzle. After the conclusion of the development, the developer composition layer is removed, and the material is then fixed, rinsed and dried. Developing treatment using a viscous treating solution has previously been known; viscous developer compositions have been used for diffusion-transfer treatment and for specific uses such as development of air photographs and of monochromatic cinema films. However, treatment with a viscous *litho*-developer has not been known.

Examples of the viscosity-increasing agents which can be used in the present invention are carboxymethyl cellulose, hydroxyethyl cellulose, sodium alginate, methyl cellulose and water-soluble polymers such as polyvinyl alcohol and copolymers of methylvinyl ether and maleic anhydride.

The viscosity-increasing agent is preferably added to the developer composition in the amount of from 0.1 to 5% weight. The viscosity of the developer composition is at least 1000 and preferably not more than 200,000 centipoises at 25°C.

The developer used in the present invention is, apart from the viscosity-increasing agent, a conventional litho-developer composition. The litho-developer of the invention is a so-called infectious developer composition which contains at least one dihydroxybenzene as the only silver halide developing agent, a water-soluble alkali, a sulphite and a sulphite ion buffer. It may also include an acid or salt such as sodium carbonate, sodium hydroxide, acetic acid and boric acid as an alkali agent or a pH buffer agent; ascorbic acid, araboascorbic acid or a salt thereof as an antioxidant; and an alkali metal halide as a development-controlling agent.

Dihydroxybenzenes are known in the art and can be easily selected by one skilled in the art. Typical examples of these compounds are hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3 - dichlorohydroquinone and 2,5 - dimethylhydroquinone; hydroquinone is preferred. These developing agents are used singly or in admixture. A suitable concentration of the developing agent is from 5 to 50 grams, preferably 10 to 30 grams per litre of the developing composition.

A sulphite ion buffer is desirably present in such an amount that the concentration of sulphite ion is maintained at a low level (preferably 0.005 to 0.05 mole per litre) in the developing composition. Examples of such buffers are an addition product of an aldehyde and an alkali metal bisulphite such as formalin-sodium hydrogen sulphite, or of a ketone such as acetone-sodium hydrogen sulphite addition product, and a carbonylbisulphite-amine condensation product such as sodium bis(2 - hydroxyethyl)aminomethane sulphonate. The addition products may be formed by reaction *in situ* by addition of its components to the compositions. The concentration of the sulphite ion buffer can be from about 13 to 130 grams, preferably 30 to 60 grams per litre of the developer.

An alkali is added to adjust the developer composition to an alkaline condition, preferably to a pH higher than 8, more preferably to a pH of 9 to 11.

The developing composition can also contain a pH-buffering agent, such as an alkanolamine, a water-soluble acid (e.g., acetic acid or boric acid), an alkali (e.g., sodium hydroxide) or a salt (e.g. sodium carbonate). Further, it may contain an alkali metal halide as a development-controlling agent. Also, it may contain an organic anti-fogging agent (e.g., benzotriazole, 1 - phenyl - 5 - mercapto - tetrazole), a polyalkylene oxide, an amine, and an organic solvent (e.g., triethylene glycol, dimethylformamide, methanol, 2 - ethoxy ethanol) in an amount of not more than 300 ml per litre of the developer composition.

As the photosensitive material for the graphic arts which are developed in the present invention, ordinary silver halide emulsions, for example, silver chloride emulsions, silver bromochloride emulsions and silver iodobromochloride emulsions can be used. In particular, a silver bromochloride emulsion or silver iodobromochloride emulsion containing not less than 50 mol% of silver chloride is preferably used. These photosensitive materials may contain hydrophilic colloidal substances as the dispersing agent for the silver halides, for example, gelatin, gelatin derivatives such as phthalic gelatin and malonic gelatin, cellulose derivatives such as hydroxyethyl cellulose and carboxymethyl cellulose, soluble starches such as dextrin and alkali starch, and hydrophilic high molecular substances such as polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamides and polystyrene sulphonic acid. Further, these photosensitive materials may contain a hydrophilic high molecular weight substance such as a polyalkylacrylate, or may contain a gelatin plasticizer such as glycerin or trimethanol propane.

The emulsions to be used in these photosensitive materials may be sensitized in known manner when they are produced (ripened) or coated. For example, the emulsions may be sensitized chemically using well-known methods, for example, by sodium thiosulphate or alkyl thiourea, by gold compounds such as a complex salt of monovalent gold and thiocyanic acid, or mixtures thereof. Further, the emulsions may contain compounds of heavy metals such as platinum, palladium, iridium, rhodium and cadmium. The emulsions may be ortho- or panchromatically sensitized by adding a colour sensitizing agent such as a cyanine dye or mercyanine dye.

The emulsions may contain a half-tone improving agent such as polyalkylene oxides and amine compounds (see United States Patent No. 3,288,612, German Patent Specification OLS No. 1,932,882 and United States Patent No. 3,345,175) and sodium benzene thiosulphate, benzotriazole or 1,3,3a,7 - tetrazaindene derivatives (United States Patent No. 3,375,114 or 3,333,959).

The emulsions may further be hardened using a hardening agent such as formaldehyde, resorcylaldehyde, dimethylol urea, 2,4 - dichloro - 6 - hydroxy - 1,3,5 - triazine (U.S. Patent No. 3,325,287) and mucochloric acid, or may contain a surface active agent such as to facilitate the application of the emulsion. The emulsions may contain a development-improving agent such as a 3 - pyrazolidone derivative and may contain a development accelerator such as a quaternary ammonium salt or cationic surface active agent.

As the support of the photosensitive materials used in the present invention, any conventional support may be used, such as of glass, cellulose acetate, polystyrene, polycarbonate, polyethylene terephthalate or resin-coated paper.

Lithographic printing plates can be prepared in known manner from the exposed and developed materials.

The treating process of the present invention has the following characteristics.

(1) The sensitivity, the quality of half-tone dots and the half-tone gradation are always uniform (they do not depend upon the number of sheets treated), since a fresh developer is always supplied to a surface of the photosensitive material.

(2) The addition of a supplemental developer composition and the use of a control strip are not required.

(3) There is no complexity of replenishment procedure, since it is not necessary to consider the fatigue and supplementing of the developer composition. Accordingly, it is not necessary to take the size of the photosensitive material to be treated and the blackened area thereof into consideration.

(4) In the viscous developer, the rapidity of air-oxidation is low in comparison with a non-viscous developer. Further, the poor stability characteristics of the litho-developer composition is not a disadvantage, because the viscous developer composition is preserved in an airtight container in order to prevent drying and oxidation and only a small area in a narrow nozzle is exposed to air at use.

(5) The treating ability does not depend upon the skill of the operator and a pre-arranged quality is always obtained, because the viscous developer composition is prepared by mixing and an automatic developing apparatus having a different degree of agitation is not used.

(6) The quality of the half-tone dots is considerably improved, since the development using the viscous developer is substantially without agitation.

(7) In using an automatic developing appa-

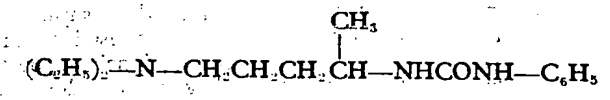
ratus, the amount of the developer composition required per sheet of the photosensitive material is large, because the volume of the liquid tank is large. However, with the viscous development treatment, the amount of the developer composition required is small and less environmental pollution is caused in disposing of the used developer.

(8) Trails (desensitization at the high density parts and sensitization at the low density parts) which occur in the treatment using an automatic developing apparatus do not occur in the viscous treatment.

The present invention will be explained by reference to the following examples. The developer compositions were prepared in an atmosphere of nitrogen to minimise oxidation thereof.

EXAMPLE 1

A silver halide emulsion comprising 75 mol% of silver chloride, 0.2 mol% of silver iodide and the balance silver bromide was subjected to gold sensitization and sulphur sensitization. The emulsion was then chemically sensitized using 3 - carboxymethyl - 5[2 - (3 - ethylthiazolinylidene)ethylidene]rhodanine. To the emulsion were added a polyoxyethylene nonylphenylether containing 50 ethyleneoxide groups per molecule, and a development-accelerating agent (described in Japanese Patent Publication No. 23465/65) of the following formula:



After also adding mucochloric acid and a polybutylmethacrylate polymer, the resulting mixture was applied to a film base to produce a litho film. This film was exposed to a sensitometry wedge through a 150-line magenta contact screen.

(a) A sample of this film was treated with a viscous developer having the following composition:

Developer Composition A	
Water	500 cc
Formalin-sodium bisulphite addition product	38 g
Hydroquinone	23 g
Sodium carbonate (monohydrate)	80 g
Potassium bromide	1 g
Carboxymethyl cellulose	20 g
Water to make	1 litre

The above-described developer composition (of a viscosity of about 1305 cPs at 25°C), kept at 27°C, was extruded using a hopper-type coater onto a surface of the film so as to apply a thickness of 150 microns. After 3 minutes, the layer of the developer was removed by a stream of water. After the film had been fixed in a fixing bath for one minute, it was washed with water and dried.

(b) For comparison, another sample of the litho film was treated at 27°C for 3 minutes employing an automatic developing apparatus FG-14L (marketed by Fuji Photo Film Co., Ltd.) using a developer having the same composition as Developer Composition A except for not containing the carboxymethyl cellulose.

The treatment (a) by the viscous developer had the following advantages over treatment (b): there was no need to be concerned with the fatigue of the developer composition and its renewal; the quality of the half-tone dots was more reproducible and was improved by one grade as compared with treatment (b); and no trails were found in the developed film.

EXAMPLE 2

As the viscous developer, a mixture having the following composition was used:

Developer Composition B	
Water	500 cc
Sodium sulphite (anhydrous salt)	30 g
Paraformaldehyde	7 g
Sodium metabisulphite	2.5 g
Boric acid	6.5 g
Hydroquinone	22 g
Potassium bromide	1.5 g
Hydroxyethyl cellulose (medium viscosity)	8 g
Sodium hydroxide to bring pH to 10.0	
Water to make	1 litre

Using the same photosensitive film element as described in Example 1, a sensitometry wedge was photographed through a 150-line magenta contact screen.

The Developer Composition B (of viscosity 1220 cPs at 25°C) kept at 27°C was spread onto a film support of the same width as the photosensitive film; an adhesive tape having a thickness of 100 microns was adhered to each edge of the support so as to stop the developer compositions from dropping off the edges thereof. The emulsion face of the exposed film was then placed on the film support and was passed between a pair of press rolls. After 3 minutes, the film was peeled off and the developer composition on the emulsion layer was removed by using a shower of a stopping solution. After fixing

for 3 minutes it was washed with water and dried.

The half-tone dots thus obtained had no fringe and the size uniformity of the small dots was excellent.

EXAMPLE 3

As the viscous developer in this Example, a mixture having the following composition was used.

Developer Composition C		
Water	400	cc
Triethyleneglycol	30	cc
Formalin-sodium bisulphite addition product	45	g
Sodium sulphite	1	g
Hydroquinone	16	g
Sodium carbonate (monohydrate	30	g
Sodium hydroxide	5	g
Boric acid		
Potassium bromide	2	g
Ascorbic acid	0.5	g
Sodium alginate	5	g
Water to make	1	litre

The Developer Composition C was placed in an airtight container. After storing the composition at room temperature for 3 months, the film was treated by the same procedure as described in Example 1; the treating ability of the developer composition was then the same as that before storage.

WHAT WE CLAIM IS:—

1. A composition for infectiously developing an exposed silver halide photographic light-sensitive material, which comprises at least one dihydroxy benzene as the only silver halide developing agent, an alkali, a sulphite, a sulphite ion buffer and an additive which increases the viscosity of the composition to at least 1000 centipoises at 25°C.

2. A composition as claimed in Claim 1, wherein the amount of the additive is 5% by weight of the developing composition.

3. A composition as claimed in Claim 1 or 2, wherein the composition has a viscosity of up to 200,00 centipoises at 25°C.

4. A composition as claimed in any preceding Claim, wherein the viscosity-increasing additive is carboxymethyl cellulose, hydroxyethyl cellulose, sodium alginate, methyl cellulose, polyvinyl alcohol, or a copolymer of methylvinyl ether and maleic anhydride.

5. A composition as claimed in any of Claims 1 to 4, wherein the developing agent is hydroquinone.

6. A composition as claimed in any of Claims 1 to 4, wherein the developing agent is chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3 - dichlorohydroquinone or 2,5 - dimethylhydroquinone.

7. A composition as claimed in any preceding Claim, wherein the sulphite ion buffer is an adduct of an aldehyde or a ketone and an alkali metal, bisulphite or is a condensation product of an amine and a carbonyl bisulphite.

8. A composition as claimed in Claim 7, which contains 13 to 130 grams of the sulphite ion buffer per litre of the solution.

9. A composition as claimed in Claim 7 or 8, wherein the composition contains 0.005 to 0.05 mole of free sulphite per litre of the solution.

10. A composition as claimed in any preceding Claim, which also contains an antioxidant.

11. A composition as claimed in any preceding Claim, substantially as hereinbefore described with reference to Composition A, B or C or Example 1, 2 or 3.

12. A method of developing an exposed silver halide photographic light-sensitive material, which comprises developing the material with a viscous infectious developer composition as claimed in any preceding Claim.

13. A method as claimed in Claim 12, wherein the light-sensitive material comprises a silver halide emulsion layer which consists of more than 50 mol% silver chloride.

14. A method as claimed in Claim 12, or 13, wherein the developing composition is prepared, and is stored before use, out of contact with oxygen.

15. A method as claimed in Claim 12 or 13 or 14, wherein the developing composition is applied to the photographic material from a vessel provided with a slit or nozzle.

16. A method as claimed in any of Claims 12 to 14, wherein the developing composition is first applied to a temporary support of at least the same area as the material to be developed, and the exposed material is then contacted with the developing composition on the temporary support.

17. A method as claimed in Claim 12 of developing a photographic material substantially as hereinbefore described with reference to Examples 1(a), 2 or 3.

18. Photographic material when imagewise exposed and then developed by a method as claimed in any of Claims 12 to 17.

19. Photographic material as claimed in Claim 18, wherein the exposure was made through a half-tone screen.

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